SCIENCE FOR CERAMIC PRODUCTION

DETONATION SYNTHESIS OF A NEW MODIFICATION OF ALUMINUM OXIDE FROM GIBBSITE BY EXPLOSION

A. I. Tsvigunov,[1] V. G. Khotin,[1] S. E. Kuznetsov,[1]
T. B. Puzyreva,[1] B. S. Svetlov,[1] and A. S. Vlasov[1]

The x-ray diffraction analysis of the condensed products resulting from explosion of gibbsite – hexogen mixtures was carried out. It was established that in explosion of the mixture, along with α-Al_2O_3, another, previously unknown modification of aluminum oxide is formed in nearly the same amount. The x-ray diffractometric data of the new modification are presented.

In was found in investigation of the Al – O system that along with the Al_2O_3 phases the gaseous phases of AlO, Al_2O, and Al_2O_2 exist above the Al_2O_3 melt. On cooling, even extremely rapid cooling, these phases decompose into Al and Al_2O_3 [1].

Among the numerous modifications of Al_2O_3, the only stable one is the α- modification (corundum) which is widely used in high-temperature construction materials.

Corundum is extremely inert in the chemical sense: it does not react with mineral acids, alkalis, and water. At temperatures of 1600 – 1800°C it does not react in an atmosphere of H_2, CO, or hydrocarbons. It should be noted that corundum is highly resistant to high-temperature carbon reduction. This is related to the extremely dense structure of corundum and to a very low deviation from stoichiometry.

The x-ray diffraction and physicochemical characteristics of metastable modifications of aluminum oxides (β-, γ-, δ-, θ-, η-, χ-, κ-, κ'-, ζ-, ϵ-) are given in [1 – 11].

The variety of metastable phases of Al_2O_3 is related to different distributions of aluminum cations among the tetrahedral and octahedral vacancies in face-centered packing.

The transition of aluminum from the tetrahedral environment (A^{IV}) to the octahedral is associated with energy variation $\Delta E(Al) = E(A^{VI}) - E(A^{IV})$, which is called the energy of octahedral orientation preference. If $\Delta E < 0$, the octahedral environment is more stable, if $\Delta E > 0$, the tetrahedral coordination is more efficient.

Analysis of published data shows that aluminum is more stable in the octahedral coordination.

Among the low-temperature metastable modifications of Al_2O_3 we distinguish γ-Al_2O_3, which is the initial product of thermal decomposition of different modifications of $Al(OH)_3$: gibbsite, bayerite, nordstrandite, boehmite γ-AlOOH, aqueous crystalline salts of aluminum: $Al(NO_3)_3 \cdot 9H_2O$, $Al_2(SO_4)_3 \cdot 18H_2O$, $(NH_4)Al(SO_4) \cdot 12H_2O$, and aluminum oxychloride [6 – 10].

Using the high-temperature Calvet calorimeter, the value of ΔE (Al) was calculated from the dissolution heats of γ- and α-Al_2O_3. It was found to be equal to 44.4 kJ/mole Al^{3+} [2].

The $Al^{IV} \rightarrow Al^{VI}$ transition is accompanied by a decrease in entropy. The $\Delta S(Al^{IV} \rightarrow Al^{VI})$ for transformation of γ-$Al_2O_3 \rightarrow \alpha$-$Al_2O_3$ according to calculations is equal to 10 J/mole · K, and according to experimental data, it is around 9 J/mole · K. A decrease in entropy in the $Al^{IV} \rightarrow Al^{VI}$ transition satisfies the condition when chemical potentials of both forms of Al in the structures in which they coexisted were equal. In sillimanite $Al^{IV}Al^{VI}SiO_5$ (on conversion to kianite: $Al^{VI}SiO_5$) the potentials of Al^{IV} and Al^{VI} become equal at a temperature of 300 – 400°C, and in γ-Al_2O_3 (γ-$Al_2O_3 \rightarrow \alpha$-$Al_2O_3$) at 2000°C [12, 13].

The γ-Al_2O_3 modification is a rare example of a metastable phase persisting nearly up to the melting point. The calculation of the Gibbs energy variation for the γ-$Al_2O_3 \rightarrow \alpha$-$Al_2O_3$ transition shows that already at 27 – 727°C, γ-Al_2O_3 transforms to α-Al_2O_3 [2].

[1] D. I. Mendeleev Russian Chemical Engineering University, Moscow, Russia.

γ-Al$_2$O$_3$ contains 1 – 2 wt.% structurally bound water which can stabilize this metastable phase. The metastable modification of γ-Al$_2$O$_3$ can be also stabilized by lithium ions [1], which partly or completely fill the octahedral vacancies. Simultaneous introduction of magnesium and lanthanum (in the ratio of 1 : 1) to the tetrahedral and octahedral positions, respectively, also has a stabilizing effect on γ-Al$_2$O$_3$. The emergence of a solid solution significantly restricts the diffusion of aluminum ions, leading to the formation of a structure based on α-Al$_2$O$_3$ [2].
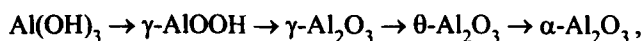
The x-ray pattern of the synthesized γ-Al$_2$O$_3$ modification in most cases corresponds to a face-centered cubic lattice with the parameter $a = 7.90$ Å (ASTM 10 – 425). According to the data in [9], a nondistorted cubic lattice of γ-Al$_2$O$_3$ should have the parameter $a = 7.906$ Å.

In certain x-ray patterns of γ-Al$_2$O$_3$ obtained from boehmite, a tetragonal distortion of the cubic lattice was observed: $a = 7.954$ Å, $c = 7.834$ Å [9].

In heating up to 800°C, γ-Al$_2$O$_3$ stabilized with water transforms into δ-Al$_2$O$_3$. In δ-Al$_2$O$_3$, ordering of vacancies in the octahedral positions is observed. This is manifested in the x-ray pattern of δ-Al$_2$O$_3$ in the form of superstructural lines. As a whole, the x-ray pattern of δ-Al$_2$O$_3$ corresponds to a tetragonal lattice in which the parameter c of a subcell is tripled: $a = 7.954$ Å, $c = 23.34$ Å [9].

At a temperature of 950 – 1000°C, δ-Al$_2$O$_3$ turns into θ-Al$_2$O$_3$ [3, 8, 9]. This transformation is related to redistribution of aluminum cations along the internodes: as in α-Al$_2$O$_3$, all aluminum in θ-Al$_2$O$_3$ occupies two-thirds of the octahedral vacancies.

As distinct from corundum, the oxygen atoms in θ-Al$_2$O$_3$, as in γ-Al$_2$O$_3$, form a cubic packing. The monoclinic C-base-centered lattice of θ-Al$_2$O$_3$ with $a = 11.813$ Å, $b = 2.906$ Å, $c = 5.625$ Å, and $\beta = 104.1°$ can be regarded as a distorted spinel lattice [11]. It was demonstrated earlier [14, 15] that in the dehydration of gibbsite according to the scheme

$$Al(OH)_3 \rightarrow \gamma\text{-AlOOH} \rightarrow \gamma\text{-Al}_2O_3 \rightarrow \theta\text{-Al}_2O_3 \rightarrow \alpha\text{-Al}_2O_3,$$

topotaxy is observed, i.e., inheritance of structural fragments by dehydration products.

Gibbsite has a laminar structure. Gibbsite laminae consist of double layers of hydroxide groups forming a slightly distorted face-centered packing in which the aluminum atoms occupy two-thirds of the octahedral vacancies. Each oxygen atom is connected with two aluminum atoms and one hydrogen atom. All aluminum atoms are surrounded by six OH groups forming a distorted octahedron linked to the others through three common edges. As a result of such association of octahedra, a hexagonal lattice is formed [16].

The parameters of the monoclinic pseudohexagonal lattice of gibbsite are as follows: $a = 8.6552$ Å, $b = 5.0722$ Å, $c = 9.7161$ Å, $\beta = 94.607°$, $V = 425$ Å^3 (ASTM 33-18).
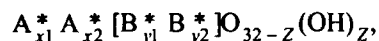
Gibbsite at atmospheric pressure is stable at temperatures below 200°C. Upon being heated, it loses water and, depending on the size of particles, it can transform into boehmite γ-AlOOH (large crystals) or into χ-Al$_2$O$_3$ (particles below 1 μm in size). The electron-pattern analysis of the χ-Al$_2$O$_3$ samples gave reason to assume that this phase crystallizes in the hexagonal singony. The lattice parameters are $a = 5.57$ Å, $c = 8.64$ Å, $V = 232$ Å^3.

Boehmite crystallizes in a rhomboid C-base-centered lattice with $a = 2.868$ Å, $b = 12.227$ Å, $c = 3.700$ Å (ASTM 21-1307). Each aluminum ion in the boehmite lattice is surrounded by four oxygen ions and two hydroxides. The rule of charge compensation requires that the octahedra [AlO$_4$(OH)$_2$] in boehmite be bound by threes. In this case, crimped layers are formed. As a whole, the structure of boehmite cannot be described based on the face-centered packing; however, inside each layer the oxygen atoms form a face-centered cubic packing. In order to transform the gibbsite structure into the boehmite structure, the Al – OH bond should be broken, and the [Al(OH)$_6$]$^{3-}$ octahedra in gibbsite should be rearranged into [AlO$_4$(OH)$_2$] octahedra, displaced from their original positions, and turned by 90° [17].

It is suggested that the conditions needed for the formation of boehmite are similar to hydrothermal [7]. It should be noted that in such conditions only one phase, that of coarsely crystalline boehmite, is formed [13].

The parameter a of the boehmite lattice is equal to one-third of the a parameter of the gibbsite lattice, i.e., the directions [100] in the lattices of both phases are preserved. The direction [100] in the lattices of boehmite and gibbsite corresponds to [110] in γ-Al$_2$O$_3$. The parameter c of the θ-Al$_2$O$_3$ lattice is twice that of the parameter a in the boehmite lattice, i.e., the direction [100] in boehmite will coincide with the direction [110] in θ-Al$_2$O$_3$.

At present, γ-Al$_2$O$_3$ and the low-temperature metastable oxides of Al$_2$O$_3$ are attributed to protospinels, i.e., compounds between the oxides and the hydroxides, with the general formula

$$A_{x1}^* A_{x2}^* [B_{y1}^* B_{y2}^*]O_{32-z}(OH)_z,$$

where A and B are tetra- and octahedral cation positions; A* and B* are nonspinel cation positions which are regarded as defects with respect to the spinel structure [2].

In studying the ZrO$_2$ – Al$_2$O$_3$ system by high-temperature diffractometry, a high-temperature modification (ε-Al$_2$O$_3$) was discovered at a temperature above 1930°C, in which 1 wt.% Al$_2$O$_3$ was replaced by ZrO$_2$. With a decrease in temperature, this modification decomposed into α-Al$_2$O$_3$ and ZrO$_2$. The diffraction pattern of ε-Al$_2$O$_3$ was indexed in a hexagonal lattice with the following parameters: $a = 7.849$ Å, $c = 16.183$ Å [4].

In the hydrothermal treatment of gibbsite with an additive of AlF_3 mineralizer, the toddite phase $5Al_2O_3 \cdot H_2O$ was obtained in [5]. After heating in vacuum (1.33×10^{-2} Pa) up to the complete dehydration temperature (750°C) and subsequent fast cooling, a metastable phase of $\kappa'-Al_2O_3$ was obtained. With further increase in temperature, $\kappa'-Al_2O_3$ transforms into $\kappa-Al_2O_3$, and then to $\alpha-Al_2O_3$. The $\kappa'-Al_2O_3$ phase as well as $\kappa-Al_2O_3$ crystallize in the hexagonal syngony. The parameters of the $\kappa-Al_2O_3$ lattice are as follows: $a = 9.599$ Å, $c = 9.024$ Å, $V = 240.2$ Å^3, density 3.68 g/m^3.

The oxygen atoms in the structure of $\kappa'-Al_2O_3$, like toddite, form a face-centered four-layer packing of the ABAC type; the aluminum atoms occupy the octahedral and tetrahedral vacancies. There are 10 2/3 aluminum atoms per one lattice cell, and the number of formula units Z is equal to 5 1/3 Al_2O_3.

The present work describes the results of the x-ray diffraction analysis of the condensed products resulting from explosion of gibbsite – hexogen mixtures. The x-ray phase analysis was performed in monochromatized radiation in a FR-552 monochromator chamber (CuK_α-radiation) and on a DRON-3 diffractometer (CoK_α-radiation). Germanium was used as a reference standard. The x-ray patterns obtained by the photographic method were measured on an IZA-3 comparator. The line intensities were estimated by the density index marks according to a 100-grade scale.

The initial compounds were hexogen crystals $C_3H_6N_6O_6$ and aluminum hydroxide powder $Al(OH)_3$ of analytically pure grade.

The needle-shaped hexogen crystals were analyzed on a SAD-4 automatic diffractometer (MoK_α-radiation, graphite monochromator). Hexogen crystallizes in a primitive rhomboid cell with parameters (Å) $a = 10.7074(0.0016)$, $b = 11.5898(0.0012)$, $c = 13.18225(0.0028)$. Our data refine the lattice parameters obtained many years ago (ASTM 5-576).

The x-ray pattern of $Al(OH)_3$ corresponds to gibbsite. All lines are indexed in a primitive monoclinic cell with parameters $a = 8.6689(44)$ Å, $b = 5.0667(20)$ Å, $c = 9.7220(41)$ Å, $\beta = 94.51°$, which corresponds to the published data (ASTM 29-41, ASTM 33-18).

The procedure of the experiments with explosive mixtures in general did not differ from that described earlier in [19]. Most of the experiments were performed in a steel shell. For comparison, several experiments were performed in a brass shell (Table 1). The bulk density of the powdered explosive mixture was 1.0 g/cm^3. All experiments involving the gibbsite – hexogen explosive mixture were performed at least three times.

According to the published data, the heat of explosive decomposition of hexogen depends on its density and varies from 1290 to 1510 kcal/kg with increase in density from 0.9 to 1.78 g/cm^3. Therefore, we thought it advisable to perform
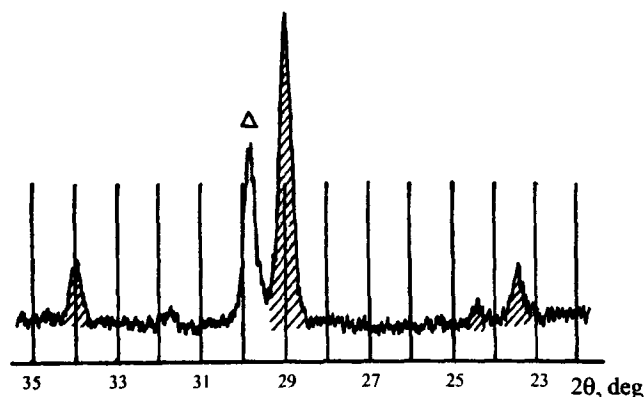

Fig. 1. A fragment of the x-ray diffraction pattern of condensed explosion products of the mixture of 30 wt.% $Al(OH)_3$ and 70% hexogen. The shaded diffraction maxima correspond to the x-ray pattern lines of the new modification of aluminum oxide with hkl 100, 110, 200, 111, and 200. The unshaded peak marked with a triangle is the corundum line with hkl 012.

several experiments with compacted samples of the explosive mixture (density 1.7 g/m^3). The process was initiated by explosion of a lead azide charge (0.1 g) placed on top of the mixture. With an $Al(OH)_3$ content of 5 – 20%, detonation of the mixture occurred, and the shell was intensely crushed. In mixtures with an aluminum hydroxide content of 25% and more, the process occurred in the form of explosive combustion, and the brass shell was only slightly inflated in the lower part. Mixtures containing over 40% $Al(OH)_3$ did not detonate in the experiment, and the initial compacted mixture remained inside the brass shell. The geometric dimensions of the shell in this case did not vary.

X-ray diffraction analysis of the condensed explosion products show that in addition to the $\alpha-Al_2O_3$ and Pb phases, another phase emerged (Fig. 1) whose content was similar to

TABLE 1

Composition of explosive mixture (wt.%)		Shell material	Phase compositions of condensed explosion products*
Al(OH)₃	C₃H₆N₆O₆,,		
10**	90**	Steel	$A_m + B_m + C$
10	90	The same	$A_1 + B_1 + C$
20**	80**	The same	$A_1 + B_1 + C$
20	80	The same	$A_1 + B_1 + C$
25	75	The same	$A_1 + B_1 + C$
30	70	The same	$A_1 + B_1 + C$
30	70	Brass	$A_1 + B_1 + C$
35	65	Steel	$A_1 + B_1 + C$
35**	65**	The same	$A_1 + B_1 + C$
35	65	Brass	$A_1 + B_1 + C$
40	60	Steel	$A_1 + B_1 + C$

* A) $\alpha-Al_2O_3$, B) the new phase; C) lead; m) much; l) little.
** Compacted mixture.

α-Al$_2$O$_3$. The amount of this phase is slightly higher in explosions of the mixtures in brass shells and for the compacted samples (Table 1).

It should be noted that the condensed product of the explosion performed in a brass shell produced clear narrow lines, especially for α-Al$_2$O$_3$. Occasionally, a very thin intense line with an interplanar distance of 3.344 Å was registered in the patterns. Evidently, this line should be attributed to graphite. It is known that hexogen in explosion decomposes into CO$_2$, CO, H$_2$O, H$_2$, and N$_2$. However, the negative oxygen balance of hexogen determines the presence of free carbon in the detonation products. The grayish-white color of the condensed products of gibbsite – hexogen explosion also points to the presence of carbon.

When the explosion was performed in a steel shell, the diffraction lines of the condensed explosion products were wider. The diffraction lines of phases produced as a result of explosion of compacted mixtures were even wider and less intense (Table 1). In this case, the explosion products had a black oily color, which pointed to the presence of a significant amount of condensed carbon in the analyzed samples.

The x-ray pattern data on the newly discovered phase (Table 2) differ from the known polymorphic modifications of Al$_2$O$_3$. The fact that this compound emerges together with

TABLE 2

Intensity	Interplanar distance, Å	hkl
14	4.413	110
6	4.238	200
100	3.584	111
25	3.493	201
20	3.071	002
10	2.592	020
12	2.523	112
18	2.488	310
5	2.211	220
2	2.007	401
10	1.982	022
16	1.933	312
14	1.859	113
7	1.846	203
2	1.797	222
5	1.632	131
5	1.589	421
5	1.562	511
1	1.504	223
5	1.475	403
2	1.451	422
2	1.451	114
5	1.429	512
5	1.330	332

α-Al$_2$O$_3$ from the gibbsite subjected to explosion makes it possible to attribute it to a new, earlier unknown modification of Al$_2$O$_3$. Perhaps, like γ-Al$_2$O$_3$, this phase is stabilized with – OH groups which were not fully removed from gibbsite in the explosion, or with the water molecules formed in hexogen explosion. This assumption is supported by the fact that after treatment of the condensed products with concentrated nitric acid, neither this phase nor lead are found in the x-ray pattern.

The nature of the arrangement of lines and the intensity ratio in the x-ray pattern made it possible to use the homology method for indexing [9]. A hexagonal lattice corresponding to the face-centered (double-layer) packing was taken as the basis for the initial lattice. In distortion of the hexagonal lattice with a face-centered packing, the lines with 001 and 002 indexes do not split. In the case where the type of distortion corresponds to a rhomboid C-base-centered lattice, the line 100 splits into two lines with indexes 110 and 200.

The intensity of the line 110 should be approximately double the line 200. The line 101 of the hexagonal lattice also splits into two lines: 111 and 201. The intensity of line 111 will be 4 times higher than the intensity of line 201. All this was observed in the x-ray pattern.

The possible combinations of indexes H_r, K_r, and L_R corresponding to the indexes of the rhomboid C-base-centered lattice can be found using the following transition matrix:

$$\begin{vmatrix} H_r \\ K_r \\ L_r \end{vmatrix} = \begin{vmatrix} 1\bar{1}0 \\ 110 \\ 001 \end{vmatrix} \cdot \begin{vmatrix} H_h \\ K_h \\ L_h \end{vmatrix},$$

where H_h, K_h, and L_h are the hexagonal lattice indexes.

All lines in the x-ray pattern of the new phase are indexed in the C-base-centered rhomboid lattice with parameters $a = 8.501(6)$ Å, $b = 5.185(4)$ Å, $c = 6.146(4)$ Å, $V = 270.9(3)$Å^3. The parameter M_{20} serves as a criterion of correct indexing [19]. In our case, $M_{820} = 23.7$. The indexing results are given in Table 2. The vectors a_r, b_r, and c_r of the rhomboid lattice are related to the vectors a_h, b_h, and c_h of the initial cell by the following relationships:

$$a_r = a_h - b_h; \quad b_r = a_h + b_h; \quad c_r = c_h.$$

In all transformations of gibbsite, a complete destruction of the lattice does not occur, especially in the direction of the axis a, in parallel to which the chains of oxygen atoms are arranged [14, 15].

Note the similar values of the parameters a and b in the lattices of the initial gibbsite and the new modification of aluminum oxide. Assuming that the aluminum oxide resulting from the gibbsite explosion has the composition of Al$_2$O$_3$, with $Z = 4$ (which corresponds to this particular lattice type), the estimated density will be 3.553 g/cm^3.

The lattice volume of the aluminum oxide modification obtained by us in the gibbsite explosion is close to the volume of the κ'-Al_2O_3 lattice. The density of Al_2O_3 composition with number of formula units $Z = 6$ will be equal to 3.75 g/cm^3.

The results of the present study do not yet make it possible to uniquely ascribe the composition of Al_3O_4 or Al_2O_3 to the new modification of aluminum oxide. Perhaps, as in κ'-Al_2O_3, part of the aluminum in the modification obtained by us is located in the tetrahedral voids, i.e., there are vacancies in the lattice.

The new modification of aluminum oxide discovered by us in the explosion products was denoted as λ-Al_2O_3.

The present work is dedicated to the memory of Professor L. M. Kovba of the Chemical Faculty of M. V. Lomonosov Moscow University, a well-known Russian scientist who made a significant contribution to the synthesis and structural research of numerous complex oxides.

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